Studies on Low Smoke Photoflash Compositions

NOTE: This article originally appeared in *Proceedings of the 19th International Pyrotechnics Seminars*, Christchurch, NZ, February, 1994.

R. Hancox, M. Wilson and B. Whiffen

Weapons Systems Division, Aeronautical and Maritime Research Laboratory (AMRL)
GPO Box 4331, Melbourne, 3001, Australia

ABSTRACT

There have been numerous reports in recent years of problems with the use of certain pyrotechnic photoflash compositions in noise simulators. The most common has been the gassing problem caused by the oxidation, during storage, of the magnesium metal fuel. In addition the quantity of particulate smoke produced by the combustion reaction can cause a number of undesirable effects when the simulators are deployed in confined environments during training operations. A study has been undertaken to investigate compositions that use alternative reactants to generate the pyrotechnic effects. The relative noise, light and smoke emissions of the compositions have been measured.

Preliminary results suggest that a formulation which uses powdered hexamine as the fuel may offer a satisfactory alternative as the filling in noise simulators.

Introduction

Pyrotechnic photoflash compositions have been used for many years in noise simulators and thunderflash devices to produce impulse noise and light effects. The compositions have been largely based on magnesium–potassium perchlorate formulations, the British compositions SR 801C and SR 813 being typical examples. A number of problems has been reported with the use of these compositions.

Firstly, the limited service life associated with devices incorporating magnesium-fuelled photoflash compositions has been well documented.[1] This is caused by the gradual oxidation of the uncoated magnesium metal powder in the presence of entrapped moisture. The reaction results in the liberation of hydrogen gas which can, in sealed devices or storage containers, cause degenerative effects (case swelling) which generally result in the failure of the devices to comply with the performance or safety specifications. As the result of several investigations at Material Research Laboratory (AMRL) it was recommended that the magnesium fuel could be replaced by aluminium powder which is less affected by moisture.[2,3] This approach was found to overcome the gassing problem and even enhance the noise and light emissions.[4]

The second problem reported by the Australian Defence Force (ADF) concerning the use of photoflash-filled devices has been the obscurating effect of the particulate smoke produced by the combustion reaction. This is of concern, particularly when the devices are fired in confined environments such as below deck on ships. The quantity of smoke produced has been found to have adverse effects on personnel and the operational requirements of training operations.

A study was undertaken at AMRL to look for alternative reactants which would maintain the noise and light emissions but reduce the quantity of smoke produced to minimal levels. After initial screening of candidate formulations was done by subjective assessment, the more promising compositions were filled into test devices and fired. The relative noise, light and smoke emissions were evaluated using instrumental techniques.

Alternative Reactants

The factors which most determine the characteristics required of the reactants for an effective impulse noise-producing pyrotechnic composition are the reaction rate achievable under pressure and the resulting temperature of the products. This tends to limit the choices to high energy reactants such as oxidants which include the alkali metal perchlorates and nitrates of potassium and barium, and the metal fuels including aluminium, magnesium, titanium and zirconium. Certain carbonaceous fuels including tetranitrocarbazole and carbon (gunpowder) have been used in noise simulators but these tend to produce large volumes of smoke.

From the operational safety aspect, the reduction of smoke emission is certainly important as is the maintenance of noise emissions within the specified noise limit criteria,[5] but the intense luminous emission from metal powder photoflash compositions can also cause operational problems including the temporary loss of vision.

The cost factor is also important in the selection of alternative reactants because practice simulators tend to be used in large numbers and hence need to be relatively inexpensive items. This would normally tend to eliminate the use of exotic (and expensive) fuels like titanium and zirconium in devices of this type unless there were significant advantages to be gained. For example the inclusion of titanium is known to increase the light output but also increases the smoke emissions.[6] It has been generally accepted that obscuration effect observed in many pyrotechnic reactions is related to the type and particle dimensions of the reaction products, particularly the metallic oxide (MgO, Al_2O_3, etc.) formed.[7] It was thus decided to investigate several carbonaceous materials, hexamine and nitrocellulose, as possible fuels and compare their performance with magnesium and aluminium.

There is probably more scope to vary the choice of oxidant. They can also contribute to the formation of particulate reaction products (smoke) and in the case of barium, the smoke tends to be toxic. It was therefore decided to investigate the use of the ammonium salts of nitrate, picrate and perchlorate (the reaction products of which are largely gaseous) and compare their performance with compositions containing potassium perchlorate.

Initial Assessment of Candidate Compositions

The study was concentrated in two main areas.

- analysis of the effects of impulse noise, light and smoke output by varying the fuel/oxidant ratio of the more conventional ingredients of photoflash compositions (aluminium and magnesium as the fuel and ammonium or potassium perchlorate as the oxidant) and,
- investigation of the effect of substituting several novel fuels or oxidants in compositions by measuring the relative impulse noise, light and smoke emissions.

The preliminary assessment of the compositions was conducted using test charges designed to contain 1.0 g of each composition. These were fixed into a jig located in an open field and fired electrically. The complete list of the systems considered in the initial assessment can be seen in Table 1. Four experienced pyrotechnicians were located at the positions marked on the layout shown in Figure 1. Each provided a subjective assessment of the emissions from each charge on a scale of 1 to 10 (1 indicating the lowest output). The compositions judged to be clearly inferior with respect to noise emission were eliminated from further study. The more promising compositions were subjected to a series of comparative assessments for light, noise and smoke output.

Table 1. Compositions Used in Initial Screening Assessment.

	Composition	Noise	Flash	Smoke	Comments
1	Mg/$KClO_4$/Acaroid (40/59/1)	10	10	10	AMRL (X) 206
2	Mg/NH_4ClO_4 (50/50)	>10	10	10	
3	Mg/NH_4ClO_4 (40/60)	10	10	10	Fuel-deficient
4	Mg/NH_4ClO_4 (55/45)	>10	10	10	Fuel-rich
5	Mg/NH_4NO_3 (48/52)	8	6	7	Unstable, NH_3 evolved
6	Mg/NH_4Picrate (50/50)	4	9	9	Low noise
7	Al/$KClO_4$/Aerosil (40/59/1)	10	10	9	AMRL (X) 210
8	Al/NH_4ClO_4 (46/54)	8	8	9	
9	Al/NH_4ClO_4 (40/60)	10	9	7	Fuel-deficient
10	Al/NH_4ClO_4 (50/50)	10	>10	10	Fuel-rich
11	Al/NH_4NO_3 (40/60)	—	—	—	Did not function
12	Al/NH_4Picrate (50/50)	—	—	—	Did not function
13	Hexamine/$KClO_4$ (15/85)	6	1	4	"sharp" report
14	Hexamine/$KClO_4$ (30/70)	7	1	6	"sharp" report

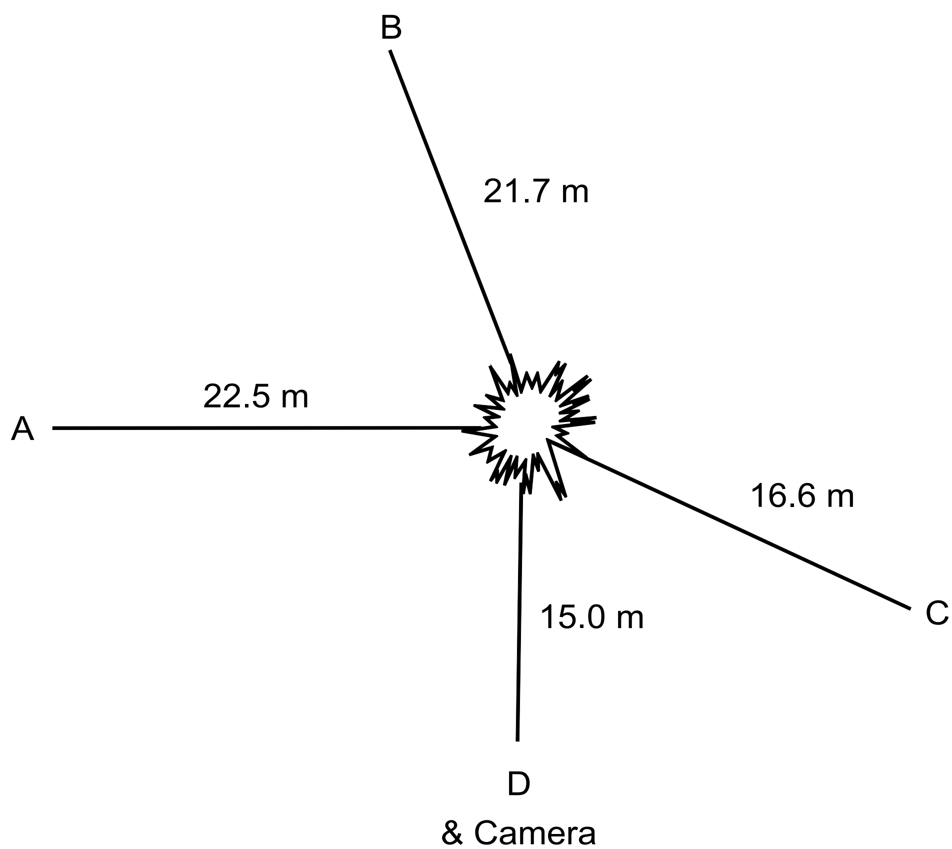

Figure 1. Sketch indicating observer positions.

Table 2. Noise Level Outputs (1 g Sample).

	Composition	Peak Pressure (kPa)	Positive Phase Duration(μs)	Impulse (kPa·s)
1	Hexamine/$KClO_4$ (15/85)	3.8	309	0.001
2	Hexamine/$KClO_4$ (30/70	4.9$^{(1)}$	226	0.001
3	Al/NH_4ClO_4 (50/50)	>9.6$^{(1)}$	458	0.002
4	Al/NH_4ClO_4 (40/60)	10.0	411	0.002
5	Al/NH_4ClO_4(37/63)	7.5	365	0.001
6	Al/$KClO_4$/Aerosil (40/59/1)	13.0	344	0.002
7	Mg/$KClO_4$/Acaroid(40/59/1)	8.7	400	0.002

(1) Only one reliable result because of fragments hitting the waveform plate.

Noise Output

Pressure gauges were mounted in the centre of two large baffle plates positioned one metre off the ground. The pressure signals were recorded on a IQ400 DSO tape recorder, later downloaded to a PC and analysed by a specially developed software package, Blast, developed at AMRL. From this, the peak pressure, positive phase duration and the impulse were determined for each sample and listed in Table 2. A typical pressure-time profile can be seen in Figure 2.

Light Output

The light emission was measured by a Spectra-Pritchard Tele-Photometer (rise time 10 μs) at a distance of 5.75 m. Calibration was conducted in the illuminance mode with a NML quartz halogen 2856 K intensity standard as the source. The voltage output of the telephotometer was recorded on a HP 400 MHz digital storage oscilloscope. Typical results of the light output measurements are listed in Table 3 and a typical light emission-time profile can be seen in Figure 3.

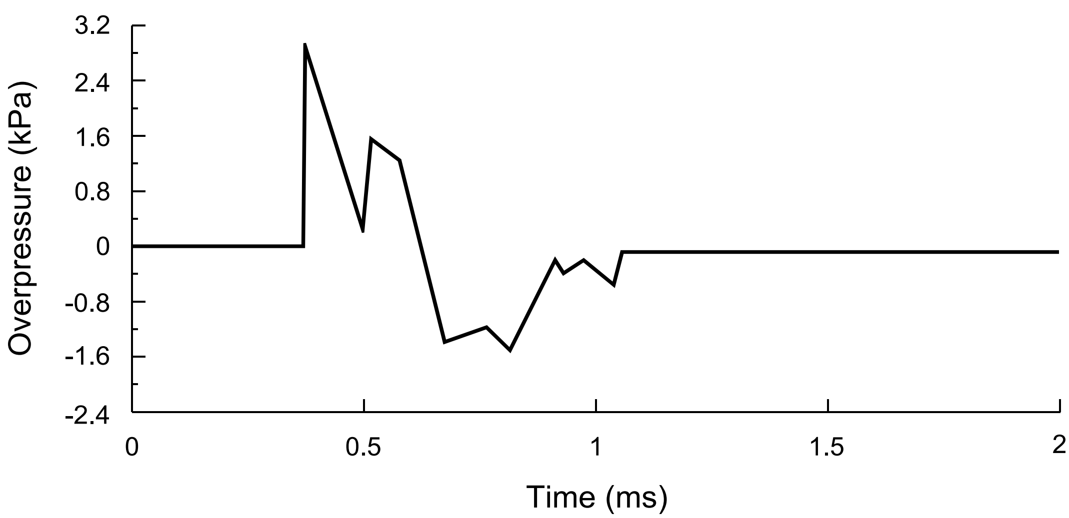

Figure 2. Pressure-time profile for hexamine/potassium perchlorate (15/85).

Table 3. Light Output of Cardboard-Cased Compositions (1 g Payload).

	Composition	Max. Intensity (cd)	Pulse Duration (ms)	Light Output (cds)
1	Hexamine/$KClO_4$ (30/70)	2.2×10^2	0.33	0.12
2	Hexamine/ $KClO_4$ (15/85)	8.3×10^1	0.13	0.05
3	Hexamine/NH_4ClO_4 (30/70)	7.2×10^1	0.40	0.02
4	Al/ NH_4ClO_4 (50/50)	8.3×10^5	2.5	2.1×10^3
5	Al/ NH_4ClO_4 (40/60)	5.3×10^5	(a)	N/A
6	Al/ NH_4ClO_4 (30/70)	2.7×10^5	<1	8.0×10^2
7	Al/$KClO_4$/Aerosil (40/59/1)	4.5×10^6	0.9	N/A
8	Mg/$KClO_4$/Acaroid (40/59/1)	1.9×10^6	0.5	N/A

(a) Incomplete records of this event.

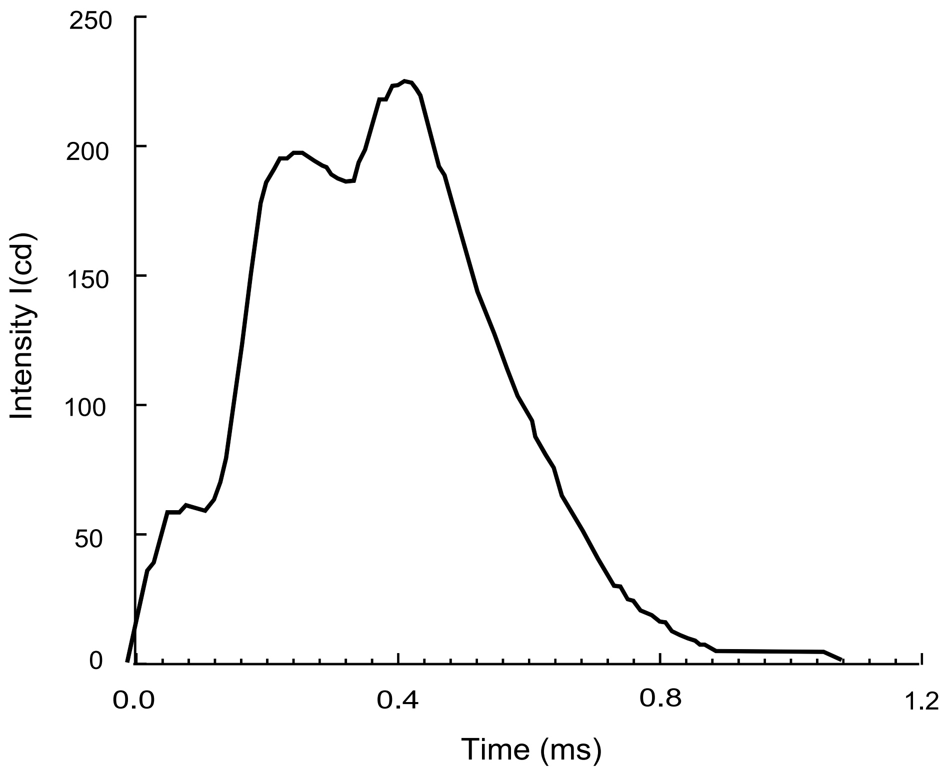

Figure 3. Light emission profile (intensity vs. time) for hexamine/potassium perchlorate (15/85).

Smoke Output

The obscuration effect of the reaction products was measured in the AMRL Smoke Chamber (Figure 4). The key features of the chamber are that it has an optical path length of 5.0 m and a total volume of 32.45 m^3. The smoke produced was allowed to circulate by the four fans situated in each corner of the chamber. The pyrotechnic systems were fired approximately 1 m above the floor of the chamber and the smoke produced from the reaction allowed to circulate for 5 minutes to achieve a uniform distribution. Loss of transmission (obscuration) was monitored with a He/Ne laser (0.6328 µm) over a prolonged period (up to 5 minutes). Obscuration data was determined for a number of

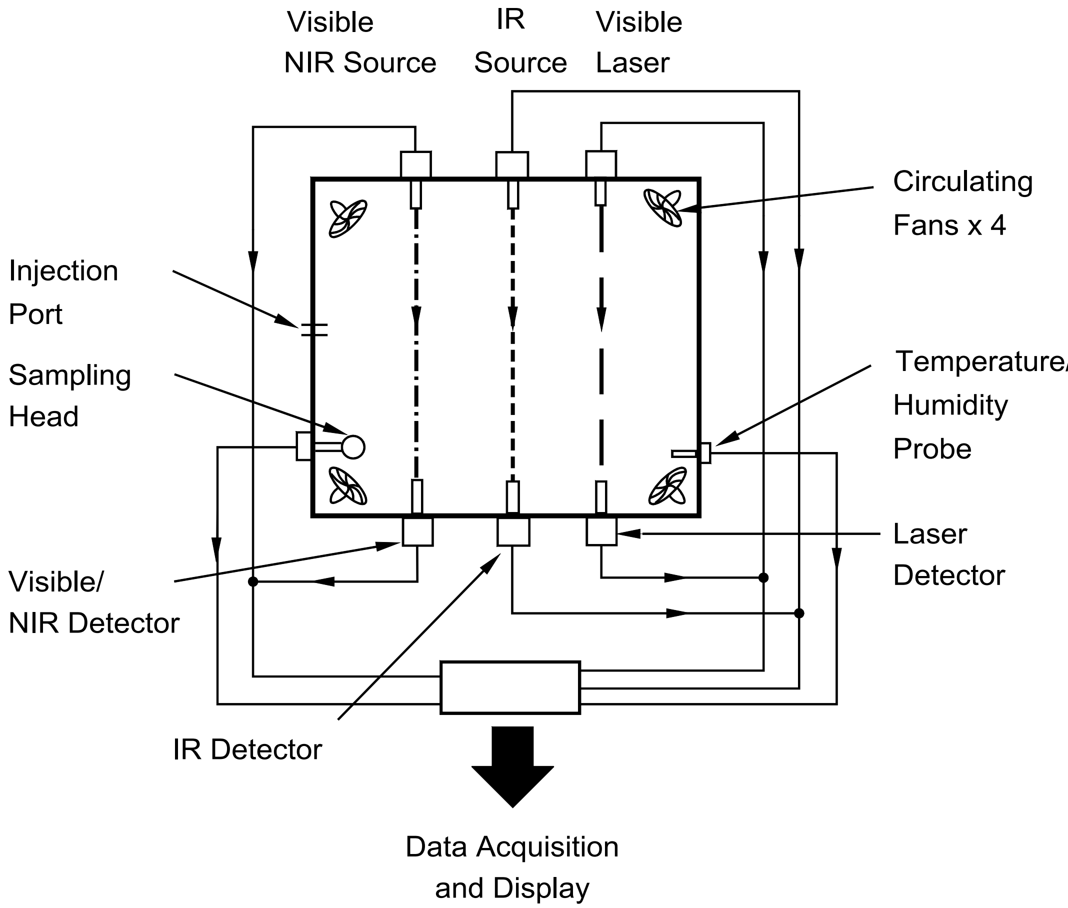

Figure 4. Schematic of the AMRL smoke chamber.

composition weights and the results for 6 g charges are shown in Figure 5.

Discussion

A survey was undertaken to study alternative fuels and oxidants that could be used in training simulators. The criteria used by the four observers was based on a relative light, noise output and smoke output. A low obscuration value was critical because it not only considered the amount of particulate matter produced but also provided an indication of the concentration of the reaction products which was important in any consideration of the possible harm that those products could cause if inhaled. This was, in effect, why serious consideration was given to such fuels as hexamine and oxidants such as nitrates and picrates because in the chemical reaction process a significant component of the reaction products are low toxic gases. Some examples are listed below:

nitrates $\rightarrow$ nitrogen

picrates, N/C, hexamine $\rightarrow$ nitrogen, CO_2

A study using the NASA-Lewis thermodynamic code has confirmed that these gases are in fact the predominant products (along with the metallic oxide) but there should be some concern that under particular fuel/oxidant ratios it is also possible to produce alternative and toxic gaseous products (e.g., oxides of nitrogen, carbon monoxide and hydrocarbons).[8] In the circumstance where the training simulator was to be used in a confined environment, this now becomes the predominant consideration.

An additional factor not able to be taken into account by the thermodynamic codes is that the fuel and oxidant may not be chemically com-

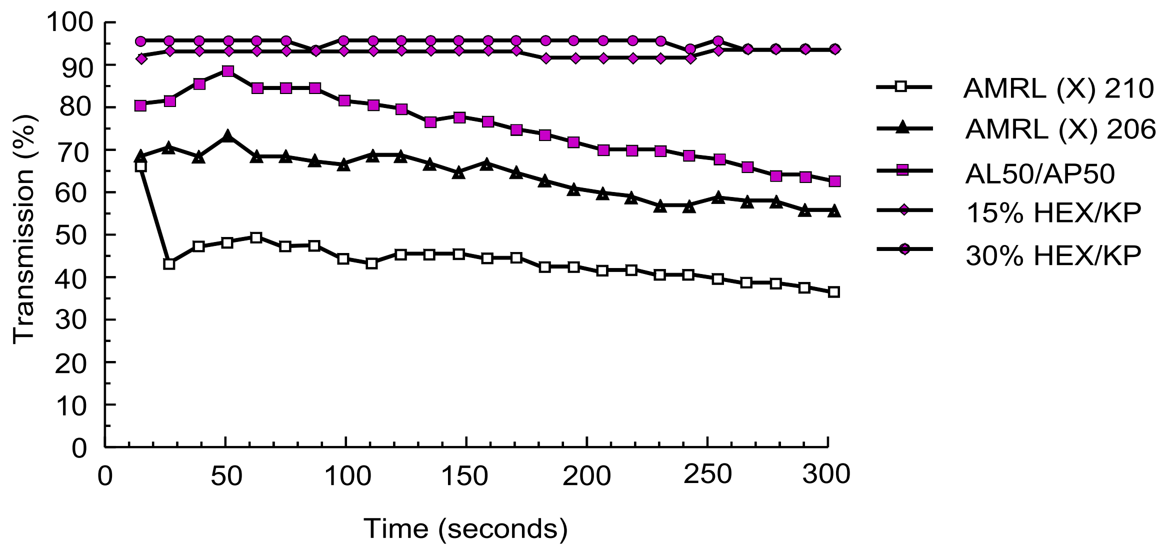

Figure 5. Smoke obscuration vs. time profiles for a range of compositions.

patible. An example was seen with the composition containing magnesium fuel and ammonium nitrate oxidant which was observed to release ammonia gas during mixing.

The most significant result can be seen in Figure 5. The more common photoflash compositions used in simulators are based on magnesium as the fuel and potassium perchlorate as the oxidant [AMRL (X) 206]. Replacement of the magnesium fuel with aluminium powder as the fuel [AMRL (X) 210] overcomes the fuel oxidation problem resulting in hydrogen evolution, but, as Figure 5 confirms, there is a significant increase in the amount of smoke produced.

However the graphs shown in Figure 5 also indicate that there is a significant decrease in the smoke output if ammonium perchlorate is used as the oxidant in place of potassium perchlorate. Traditionally ammonium perchlorate is not used widely in pyrotechnics, and there are several reasons for this. Firstly it tends to be hygroscopic, and hence its use would result possible reduction in service life. Secondly and perhaps more importantly, it is generally regarded as a more explosively hazardous component especially if the system is vulnerable to contamination or incompatibility. Recent studies in propellant technology have reported an improved processing capability and chemical and thermal stability using certain binders (e.g., 0.5% Aziridene) to coat the ammonium perchlorate.[9] Its use in pyrotechnic applications has yet to be explored. Even if improved stability and decreased explosive sensitiveness can be obtained by the coating of the ammonium perchlorate, in pyrotechnic applications there is a maximum loading of binder or diluent that can be added before the system no longer functions as designed. For example, in the development of composition, AMRL (X) 210, the flow properties were found to be considerably improved with the addition of 1% of Aerosil.[4] If the Aerosil content was raised above 3% it was observed that the pyrotechnic performance of the composition was degraded.[10]

As mentioned earlier, one of the complaints with aluminium-based photoflash composition has been that the light output has been sufficient to cause temporary flash blindness. This situation is not ideal for training simulators. Results obtained with aluminium/ammonium perchlorate composition indicate that there is no significant decrease in the light output when compared with AMRL (X) 210.

Conclusions

A preliminary study has been undertaken to investigate the use of alternative reactants in training simulator compositions. The main problems with the existing systems have been the rapid oxidation of the magnesium fuel and the increased light and smoke emissions of the aluminium-based compositions.

The initial findings have indicated that there are some advantages (lower smoke at similar noise output) by replacing the potassium perchlorate oxidant with ammonium perchlorate. There are a number of disadvantages associated with the use of ammonium perchlorate in pyrotechnic systems (moisture sensitivity, chemical instability and increased explosive sensitiveness) but more recent processing techniques have been developed (coating of the AP) which have helped to overcome many of those problems.

The results also indicated that the use of non-metallic fuels such as hexamine can certainly reduce the smoke output with only a relatively small reduction in noise output. As a result of this study, one of the outcomes may be to used separate fillings in noise and light simulators.

Acknowledgments

The authors wish to thank Mr. F. Fitzsimons and Mrs. D. Bajada for their assistance with the obscuration measurements, Mr. T. Fagan who conducted the pressure measurements and Optical and Photometric Technology P/L who conducted the light emission measurements.

References

1) M. Capp, *The Moisture Absorption Process of Certain Pyrotechnic Compositions*, MQAD Technical Paper 734, Materials Quality Assurance Directorate, Woolwich Arsenal, London, UK, 1980.

2) M. A. Wilson and R. Bird, *Defect Investigation of Cartridge, Illuminating, 1-1/2 inch*, AMRL-TN-501, Maribyrnong Research Laboratory, Australia, (U), 1986.

3) S. Murdoch, *Defect Investigation of Thunderflash Mk N5*, AMRL-TN-522, Materials Research Laboratory, Melbourne, Australia (U), 1987.

4) M. Wilson, *The Development of Pyrotechnic Photoflash Composition AMRL (X) 210*, AMRL-TR-89-16, Materials Research Laboratory, Melbourne, Australia (U), 1989.

5) *CHABA, Proposed Damage-Risk Criterion for Impulse Noise (Gunfire)*, W Dixon Ward, Ed., Report of Working Group 57, NAS-NRC Committee on Hearing, Bioacoustics and Biomechanics, July 1968.

6) K. Ramohalli, "Combustion Modelling of Explosive Pyrotechnics", *Proceedings of the 19th International Annual Conference of ICT*, Karlsruhe, Germany, June 29–July 1, 1988.

7) K. Ramohalli, "Modeling the Smoke (Cloud) and Noise from Aluminium-Magnesium Pyrotechnics", *Proceedings of the 10th International Pyrotechnics Seminar*, held in conjunction with 16th International Annual Conference of the ICT, Karlsruhe, Germany, July 2–5, 1985.

8) L. de Yong, (AMRL), Unpublished results.

9) P. F. Alello, R. W. Hunter, A. P. Manzara, "Room-Temperature Storable Bonding Agent", *Proceedings of the 27th International Annual Conference of ICT*, Karlsruhe, Germany, 1996.

10) M. Wilson, (AMRL), Unpublished results.